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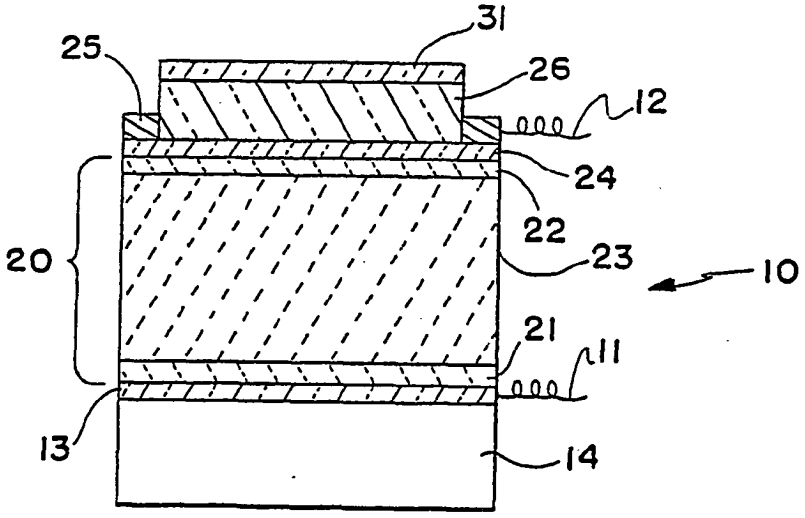

(57) Abstract

Relatively weak light signals are detected by a reverse biased photodetector (10, 30, 50, 70) that is a semiconductor diode including a transparent, electrically conductive front contact (24) formed of a thin film of a transparent, electrically conductive oxide, a body (20) of disordered silicon including three layers (21, 22, 23), the outer layers (21, 22) being oppositely doped and the central layer (23) being substantially intrinsic, and a second, rear contact (13) disposed on silicon body (20) opposite the front contact (24), and monitoring changes in the current flowing through the reverse biased diode relative to the dark current of the diode. In order to achieve desired quantum efficiencies in the spectral region from 200-400 nm, the oxide film is less than 50 nm in thickness and most preferably is about 15 to 30 nm in thickness. The photodetection method is particularly effective at elevated temperatures where its noise is significantly less than that of known photodetectors.

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LOW NOISE PHOTODETECTION AND PHOTODETECTOR THEREFOR

TECHNICAL FIELD

This invention relates to photodetectors, and more particularly to crystalline silicon photodetectors for the detection of light in the ultraviolet region of the electromagnetic spectrum.

BACKGROUND ART

Crystalline silicon photodetectors have been widely used for the detection of light in the visible and near infrared regions of the electromagnetic spectrum. Unless special structures are employed, the crystalline silicon photodetectors generally do not respond well in the ultraviolet (UV) region of the electromagnetic spectrum.

Ultraviolet light detectors have become of increasing importance with the development of short pulse lasers producing electromagnetic radiation in the ultraviolet or near ultraviolet wavelength region of the electromagnetic spectrum.

Crystalline silicon ultraviolet detectors typically include an intrinsic, i.e., effectively undoped, region sandwiched between oppositely doped, i.e., one p-type and one n-type, layers. The light to

be detected enters through one of the doped regions and some of the unabsorbed light that reaches the intrinsic region produces charge carriers that are collected as an indication of the presence of ultraviolet light. The response and efficiency of these crystalline detectors are limited by the quantity of light absorbed in the "front" doped region through which the light must pass in order to reach the intrinsic region.

In order to achieve the doping level necessary for good performance, that "front" doped region must have a thickness of several hundred nanometers (nm), but the strong absorption of ultraviolet light in a crystalline front region of that thickness limits the quantum efficiency of crystalline silicon detectors. In addition, crystalline silicon detectors show some instability after exposure to ultraviolet light.

Crystalline silicon photodetectors exhibit dark currents, i.e., the current that flows when a reverse bias voltage is impressed on the diode and no illumination falls on the diode, that become, for many applications, unacceptably large. Generally, a large dark current implies a relatively large noise level. As noise level increases, the sensitivity of a photodetector necessarily declines.

Because of the poor UV spectral response of crystalline silicon photodetectors, and to overcome the quantum efficiency limitations in crystalline

silicon ultraviolet light detectors, materials other than silicon are employed in some ultraviolet detectors. For example, Schottky barrier photodiodes employing gallium arsenide phosphide are commercially available and are sometimes employed as UV detectors. The Schottky barrier photodetectors exhibit desirably low dark currents and good UV stability. However, these results are achieved at the expense of UV sensitivity. Furthermore, these alternative material photovoltaic detectors of ultraviolet light are expensive because of the materials employed.

Other ultraviolet light detectors are also known. A summary of the state of the art appears in two articles by Wilson and Lyall published in 24 Applied Optics 4530-4546 (December 1986). None of the available detectors achieves low cost, long term stability and high efficiency.

Accordingly, it would be useful to provide a low cost, high efficiency, solid state, photovoltaic detector of ultraviolet radiation that is stable over time. In addition, there is a need for a photodetector and a photodetection method that can be used in any selected region of the electromagnetic spectrum. from UV to infrared, and that has low noise characteristics to maximize sensitivity. Preferably, the photodetector and method of photodetection are usable at elevated temperatures where the dark currents of known photodetectors increase unacceptably.

DISCLOSURE OF THE INVENTION

In the invention a low noise, solid state, photovoltaic detector for detecting relatively weak light signals employs a body of amorphous silicon. Electrical contacts are disposed on opposite sides of the structure, including, on the light incident side, a thin, transparent, electrically conductive light-transmissive film of an electrically conducting oxide, such as tin oxide or indium oxide doped with tin. In order to maximize quantum efficiency, the oxide film is no thicker than about 50 nm and, most preferably, is about 15 to 30 nm thick. The oxide film forms a first contact.

In one embodiment, the amorphous silicon body includes a p-i-n structure. The silicon body includes three layers serially disposed on the first contact, transversely to the direction of incident light, including two outer layers doped n-type and p-type, respectively, and a central layer that is substantially intrinsic in conductivity type. A second contact is disposed on the silicon body opposite the first contact. In this embodiment, the doped amorphous silicon region adjacent the oxide film is only tens of nanometers thick so that little ultraviolet is lost in the doped front region. As a result, detector efficiency is improved, even over that achieved with exotic materials such as gallium arsenide phosphide.

Preferably, the front doped layer is a doped microcrystalline form of amorphous silicon.

When employed as a photodetector, a reverse bias voltage is impressed across the diode through the first and second contacts and changes in current flowing through the diode are measured. Changes in that current with reference to the dark current of the diode are an indication of the presence of incident light and of its intensity.

A p-i-n photovoltaic detector according to the invention may be disposed on a glass substrate coated with a conductive tin oxide film as a rear contact or may be directly disposed on an electrically conducting substrate, such as a metal, a metallic alloy like stainless steel, or silicon, that forms the rear contact. Because of the relatively strong absorption by amorphous silicon of ultraviolet light, the light-absorbing intrinsic region need be no more than about 250 nm in thickness, but may be thicker.

An encapsulated embodiment of the invention includes a header or other support on which a p-i-n amorphous silicon photovoltaic detector is disposed. The header provides the back electrical contact and an oxide film provides the front electrical contact. This embodiment is prepared by depositing the oxide film on a quartz substrate and then attaching the detector to a header for encapsulation.

In yet another embodiment of the invention, the amorphous silicon body is a doped film disposed on a crystalline silicon layer of the opposite conductivity type. Because the amorphous silicon film absorbs less ultraviolet light than a crystalline counterpart, the sensitivity is enhanced over that of a totally crystalline detector.

In the invention, because of the extreme thinness of the front oxide layer, it is important that the oxide have a relatively low resistivity. In addition, it is desirable to deposit a highly conductive, metallic current collection layer on a portion of the oxide layer. The optical transmission characteristics of the oxide film can be altered by depositing on it another film or films of transparent materials such as silicon dioxide, silicon nitride, magnesium fluoride or calcium fluoride.

The first layer of the silicon body upon which light falls may be microcrystalline for good transmission of light to the substantially intrinsic layer. Alternatively, the silicon body may be amorphous silicon throughout. The thickness of the layers of the silicon body and of the first contact may be adjusted to improve photodetector sensitivity in a selected spectral region. The photodetector may be connected to an amplifier that is disposed on the same mounting body with the detector to reduce the length

of interconnections between the amplifier and photodetector to combat noise and to maintain the detector and amplifier at similar temperatures.

Photodetectors and photodetection according to the invention exhibit, at room temperature, lower noise than crystalline silicon photodetectors and noise levels comparable to those of gallium arsenide phosphide photodetectors. As the temperature of the photodetector increases, the novel devices and method exhibit far lower noise than the known photodetectors.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a sectional view of an ultraviolet responsive device according to the invention;

FIG. 2 is a sectional view of another embodiment of an ultraviolet responsive device according to the invention;

FIG. 3 is a sectional view of a third embodiment of an ultraviolet responsive device according to the invention;

FIG. 4 is a graph of the quantum efficiency as a function of wavelength of various ultraviolet responsive devices including some devices according to the invention;

FIG. 5 is a graph of the quantum efficiency of a device according to the invention and having a

relatively thick light-absorbing layer, before and after exposure to sunlight and of a reference ultraviolet responsive device.

FIG. 6 is a graph of the quantum efficiency as a function of wavelength of a device according to the invention and having a light-absorbing layer, before and after exposure to sunlight and ultraviolet light and of a reference ultraviolet responsive device.

FIG. 7 is a sectional, schematic view of another embodiment of a photodetector according to the invention.

FIG. 8 is plot of dark current density versus voltage for several photodetectors including a photodetector according to the invention.

FIG. 9 is a plot of the reverse bias voltage versus current characteristics of a photodetector according to the invention as a function of temperature.

FIG. 10 is a plot of the current versus reciprocal temperature characteristics of a photodetector according to the invention as a function of reverse bias voltage.

FIG. 11 is a schematic diagram of circuitry employed in comparing the noise characteristics of the novel photodetector to the noise characteristics of known photodetectors.

FIGS. 12A and 12B are plots of the calculated noise currents of the novel photodetector and of known photodetectors for different frequency bandwidths as a function of temperature.

BEST MODE OF CARRYING OUT THE INVENTION

Three embodiments of structures of novel photovoltaic devices are illustrated in cross section in FIGS. 1, 2 and 3. Each of these devices is photovoltaic. That is, each device produces an electric current and/or a voltage in response to the incidence of electromagnetic radiation, particularly in the ultraviolet portion of the spectrum. As with other photovoltaic devices, the ultraviolet responsive devices of the present invention may be operated with or without an external voltage applied. In the former case, the incidence of ultraviolet radiation is indicated by the generation of an open circuit voltage or a closed circuit current flow. In the latter case, an external voltage is impressed across the electrical contacts of the device to enhance current collection. The external voltage creates an electric field within

the device that aids in collecting charge carriers produced within the device in response to the incidence of ultraviolet radiation. As used here, the term ultraviolet radiation means short wavelength light that is not visible to the naked eye, particularly in the spectral wavelength range from about 200 nm to 400 nanometers (nm).

The ultraviolet responsive device 10 of FIG. 1 includes electrical terminals 11 and 12 for external electrical contact to the device. Terminal 11 is connected to an electrically conductive layer 13 that is referred to as the rear contact. The rear contact lies at the deepest portion of the device with respect to the direction of incident electromagnetic energy. Layer 13 is an electrically conductive material either in the form of a film or a bulk material. For example, contact 13 may be a thin layer of tin oxide that is disposed on an electrically insulating substrate 14 that provides mechanical support. For example, substrate 14 may be glass. Substrate 14 may also be a metal header and layer 13 may be a metal alloy, an adhesive or another material that forms an ohmic contact and/or mechanical bond between substrate 14 and an amorphous silicon body 20. Alternatively, as indicated in FIG. 2, contact 13 may be a metal, a metal alloy such as stainless steel, or crystalline or polycrystalline silicon directly in contact with amorphous silicon body 20.

Amorphous silicon body 20 includes two oppositely doped regions 21 and 22 sandwiching an intrinsic region 23. Body 20 is disposed on contact 13. Regions 22, 23 and 21 are arranged serially so that incident light passes through them in that order. For clarity, FIG, 1 (and FIGS. 2 and 3) are not drawn to scale. Generally, the doped regions 21 and 22 are very thin, on the order of 10 nm. One of those regions incorporates an impurity, giving it a p-type conductivity, and the other region incorporates a different impurity, giving that region an n-type conductivity. Region 23 contains either no impurity or some compensating impurity that provides that region with a relatively high resistivity that may be weakly n-type or p-type in conductivity character, but substantially favors neither of those types of conductivity.

As understood in the art, the amorphous silicon described here contains hydrogen and/or another dangling bond terminating element in a sufficient concentration so that its electronic qualities are acceptable for the novel ultraviolet detector. That is, the amorphous silicon is of the same type and quality required for solar photovoltaic applications. As used here, the term amorphous silicon encompasses not only the traditional amorphous material that lacks any long-range atomic order, but also microcrystalline materials that contain tiny crystallites within a

surrounding disordered matrix. Preparation of microcrystalline silicon is well known and was described, for example, by Vanier, et al. in 66 J. of NonCrystalline Solids 31ff (1984).

In accordance with the usual operation of an amorphous p-i-n photovoltaic structure, incident light passes through the front region, here region 22, without substantial absorption and generates charge carriers in region 23. By virtue of the built-in electric field inherently produced by the structure, or as enhanced by an external voltage applied across terminals 11 and 12, those charge carriers are attracted from region 23. Most of those light-generated carriers are collected in regions 21 and 22 and produce either a voltage at terminals 11 and 12 or a current flowing through those terminals. Generally, region 23 is substantially thicker than regions 21 and 22 because it is desired that most of the light absorption and charge generation take place in region 23. Region 23 is preferably on the order of 250 nm in thickness, but may be thicker or thinner.

Microcrystalline silicon has better light transmissivity, i.e., lower absorption, and is generally more easily doped than totally disordered silicon. Therefore, it is preferred in some embodiments of the invention that region 22, the front or window region, be microcrystalline silicon. The window region may be either p-type or n-type and may be

heavily doped so as to be referred to as p+ or n+. In addition, carbon or nitrogen may be added to the window region to increase its energy band gap. The additional element can be advantageously used to form p+ amorphous silicon carbide or n+ amorphous silicon nitride without the necessity of achieving perfect stoichiometric proportions. The increased band gap reduces light absorption in the window region.

A thin film 24 of an electrically conducting, light-transmissive material is disposed on body 20 opposite layer 13 as a front contact. Thin film 24 is adjacent to and in touching contact with region 22 of body 20. Film 24 is referred to as the front contact since it lies at the top of the device with respect to the direction of the incident light. The function of film 24 is to provide an electrical contact for terminal 12 of the device, yet to absorb as little ultraviolet light as possible in order not to reduce the sensitivity of the device.

An appropriate material for thin film 24 is a light-transmissive, electrically conducting oxide. Preferred oxides are indium oxide doped with a metal, preferably tin, and tin oxide. Indium tin oxide (ITO) is preferred when the oxide film is deposited after the amorphous silicon body has been deposited, because ITO can have a lower resistivity than tin oxide. However, when the device is prepared by depositing the amorphous silicon body on the front contact, a tin

oxide film is preferable over ITO. Indium in an oxide film can dope or otherwise adversely affect the subsequently deposited amorphous silicon body and is preferably avoided. Conversely, depositing microcrystalline silicon on an oxide film can adversely affect the film. Therefore, when the amorphous silicon body is deposited on an oxide film, it is preferred that microcrystalline silicon not contact the oxide film.

It is important that oxide film 24 be very thin, less than 50 nm and, most preferably, about 15 to 30 nm, in thickness. Because film 24 is so thin, it is important that its electrical conductivity be as high as possible to minimize resistive losses when current flows laterally through the film. To enhance current collection and minimize resistive losses, a metallic current collector 25 is disposed on part of film 24 opposite body 20. Current collector 25 occupies as little of the surface of film 24 as possible to limit obscuring of body 20 from incident ultraviolet light. Collector 25 may be in the form of a grid or, more preferably, may be peripherally disposed around the area of the novel detector. For example, collector 25 may be annular in a device having a circular cross section transverse to the direction of incident light.

FIG. 1 also illustrates a second embodiment of the invention that permits easy encapsulation. In FIG. 1, a glass substrate or superstrate 26 is shown

lying over and in contact with film 24. Superstrate 26 must be highly transparent to ultraviolet light if the detector is to function as intended. High silica content glass, such as quartz, may be used as superstrate 26. In this embodiment, the detector is constructed in reverse order from the embodiment described above. Film 24, which, as mentioned above, is preferably tin oxide in this embodiment, is deposited on superstrate 26. Thereafter, amorphous silicon body 20 is deposited by a conventional glow discharge technique. As discussed, it is preferable in this embodiment that the region of silicon body 20 contacting film 24 not be microcrystalline. However, the amorphous silicon region contacting the oxide film may contain a band gap increasing agent, i.e., may be amorphous silicon carbide or amorphous silicon nitride.

In this alternative embodiment of FIG. 1, substrate 14 may be a conventional semiconductor device header. Layer 13 may be an electrically conducting metal alloy or adhesive that forms an ohmic contact and mechanical bond between silicon body 20 and header 14. Alternatively, an electrically insulating mechanical bond might be formed between layer 13 and a header. Wires extending from the front and rear contacts may be bonded to electrically conducting posts extending from the header.

The header mounted device can be enclosed in a container bonded to the header or encapsulated in an electrically inert material in accordance with long established processes. As discussed in more detail below in connection with FIG. 2, one or more anti-reflection transparent layers 31 may be deposited on superstrate 26 opposite film 24. Calcium fluoride and magnesium fluoride may be employed in anti-reflection films 31.

Another embodiment of an ultraviolet detector 30 according to the invention is shown in cross section of FIG. 2. (In all figures like elements are given the same reference numbers.) In device 30, rear contact 13 comprises an electrically conductive material that also provides mechanical support, i.e., is a substrate. Rear contact 13 may be a metal, a metallic alloy such as stainless steel, or single crystal or polycrystalline silicon. Particularly when rear contact 13 is crystalline silicon, its surface on which the amorphous body 20 is disposed may be textured or grooved to diffuse incident ultraviolet radiation that reaches the contact and is reflected from it. Since most of the incident ultraviolet light is absorbed before reaching the rear contact, texturing is most effective in trapping externally incident light rather than internally reflected light. A textured or grooved substrate can produce surface features in the amorphous silicon body and oxide

layer. Reflected incoming light may strike a surface of a feature one or more times improving the probability of its absorption. Texturing of a crystalline rear contact may be achieved by chemically etching the contact with a preferential etch to expose crystalline planes lying at oblique angles. These etches generally produce pyramidal facets. Alternatively, grooves can be formed with chemical etching of selected areas using conventional lithographic processes.

In detector 30, a second light-transmissive film 31 has been deposited on thin film 24. The thicknesses and the respective indices of refraction of films 31 and 24 affect the optical characteristics of the light-transmissive layer they comprise. By adding film 31, the layer comprised of films 24 and 31 can be optically tuned. In that tuning, optical interference effects can be employed to reduce reflection of particular wavelength ranges of the electromagnetic spectrum. Use of optical interference effects in thin films is well understood in the art. Film 31 may be composed of one or more strata of a number of light-transmissive materials such as silicon dioxide, silicon nitride, magnesium fluoride or calcium fluoride. Single or multiple overlying, anti-reflection films can also be used with the devices of FIGS. 1 and 3.

A third embodiment 50 of an ultraviolet detector is shown in cross section in FIG. 3. Detector 50 includes a crystalline silicon substrate 13 with a deposited metal contact 36 to which terminal 11 is electrically attached. Contact 36 may be an aluminum film annealed to form an ohmic contact and/or back surface field reflector. Amorphous silicon body 20 is a film of a particular conductivity type. Silicon substrate 13 is of the opposite conductivity type from body 20 so that a rectifying junction is established between them. A conductive oxide layer 24 is disposed on amorphous body 20.

Like films 24 in detectors 10 and 30, light-transmissive film 24 in detector 50 is no more than 50 nm thick and is preferably about 15 to 30 nm in thickness. Because doping efficiencies in amorphous silicon are higher than in crystalline silicon, body 20 can be relatively thin, about 10 nm, without sacrifice in performance. The thinness of body 20 reduces light absorption so that overall performance is improved over a totally crystalline detector. As described in connection with detectors 10 and 30, it is preferred that body 20 in detector 50 be microcrystalline silicon to lower its light absorption compared to that of totally disordered amorphous silicon. Body 20 may also contain a band gap increasing agent such as carbon or nitrogen. Body 20 may be heavily doped to form a p+ or n+ region. Most preferably, body 20 is a

microcrystalline n+ region and substrate 13 is a p-type silicon.

As already described, body 20 may contain pyramidal facets or grooves in order to improve performance. These textures aid in the capture of incident light by producing multiple reflections that ultimately direct light into the substrate that would otherwise be lost. These textures can be formed as described above in connection with FIG. 2.

A particular advantage of the amorphous/crystalline silicon embodiment 50 of the invention lies in its wide spectral response range. Because crystalline silicon has an inherent red response, the amorphous/crystalline silicon device has a response that extends from the ultraviolet, through and beyond the visible range. This embodiment is a wide spectral response electromagnetic energy detector.

Amorphous silicon photovoltaic devices having two general structures, both similar to devices 10 and 30, yet substantially different from the present invention, have been employed for sometime for converting sunlight to electricity. However, both of those known types of solar photovoltaic devices are unsatisfactory as ultraviolet light detectors.

One type of those solar cells uses an opaque substrate on which an amorphous silicon p-i-n device

is disposed. Those devices generally include a relatively thick ITO contact. That front contact is at least 60 nm in thickness, and usually is thicker. This relatively thick film is employed to reduce resistive current collection losses that can be experienced in thin films and to avoid optical interference effects in the visible light spectrum. However, the ultraviolet light absorption characteristics of ITO prevent efficient transmission of the incident ultraviolet light through layers 60 nm or more in thickness. Ultraviolet light absorbed in the front contact cannot enter these devices and therefore cannot generate any useful photovoltaic response to ultraviolet light. The failure of amorphous silicon solar photovoltaic cells of this type as ultraviolet light detectors is demonstrated in FIG. 4.

The other known amorphous silicon solar cell structure conventionally employs a non-quartz glass substrate, a tin oxide film and a p-i-n structure, receiving light in that order. Because the conventional glass substrate and tin oxide film are, together, strong absorbers of ultraviolet light, little of it can reach the photovoltaically active amorphous silicon.

In FIG. 4, the measured quantum efficiency of various structures is plotted against the wavelength of incident light. These response characteristics were measured by training light of a narrow

bandwidth on the various tested devices and scanning the wavelengths of the incident light over the range indicated on the abscissa, namely from 200 nm to about 800 nm. As noted above, the region of interest is the non-visible ultraviolet light region from 200 nm to 400 nm. The quantum efficiency is plotted on the ordinate in relative terms representing the number of electrons generated for each incident photon. To provide a reference response, the characteristics of a commercially available Schottky barrier, gallium arsenide phosphide ultraviolet detector were measured. That measured reference response is plotted as curve a in FIG. 4. The gallium arsenide phosphide Schottky barrier detector was manufactured in Japan by Hamamatsu.

Photovoltaic structures according to the invention were prepared employing glass substrates coated with tin oxide on which an amorphous silicon body was deposited. The amorphous silicon body was deposited by a conventional glow discharge technique. Regions of n-type, intrinsic and p-type amorphous silicon were deposited in that order. The intrinsic regions deposited ranged from about 250 to about 500 nm in thickness. Because of the light absorption characteristics of amorphous silicon, essentially no more light is absorbed in a 500 nm intrinsic region than is absorbed in a 250 nm intrinsic region. As discussed below, thinner intrinsic region devices

exhibit better stability than detectors with thick intrinsic regions.

The response curves of FIG. 4 were obtained from devices having 500 nm thick intrinsic regions. The doped regions were about 10 nm thick. A high quality layer of ITO was deposited on top of the p-type amorphous silicon. The ITO had a resistivity of about 2 x 10^{-4} ohm-cm. Different thicknesses of ITO films as front contact were deposited on the amorphous silicon bodies. In FIG. 4, the response curves correspond to the respective thicknesses of the front contacts:

Curve	ITO Thickness (nm)
b	50
c	30
d	20
e	12.5

Focusing on the responses in the spectral region from 200-400 nm, it can be seen that for over half of that range quantum efficiencies are lower for curves b and c than for the reference gallium arsenide phosphide device, curve a. By contrast, the quantum

efficiencies represented by curves d and e are, over the spectral region of interest, substantially the same as or better than that of the reference gallium arsenide phosphide device. Curve c shows quantum efficiencies over the upper half of the spectral range of interest that are so much better than the reference detector that they compensate for the poorer response in the lower half of the range.

Curves c, d and e demonstrate that ultraviolet detectors in accordance with the invention can be constructed providing improved sensitivity and quantum efficiencies compared to those of the reference device, provided the ITO front contact has a thickness not exceeding about 50 nm. Substantially improved quantum efficiencies and sensitivities are achieved if the ITO thickness is about 15 to 30 nm. These results further demonstrate that conventional amorphous silicon photovoltaic cells having ITO front contacts at least 60 nm in thickness are not useful as ultraviolet light detectors.

It is well known that many amorphous silicon devices show changes in performance upon lengthy exposure to solar energy. While the devices of the present invention are generally not directed to the absorption of light from the solar spectrum, an embodiment of the invention was exposed to a standard AM1 simulated solar spectrum. (AM1 solar radiation represents light having the intensity and spectral content

reaching the surface of the earth when the sun is positioned at the zenith transmitting its light through a standard atmosphere.) Response curves a and e representing the quantum efficiency of the reference device and of an embodiment of the invention employing an ITO front contact of 125 nm thickness, respectively, are plotted in FIG. 5. These are the same response curves that appear in FIG. 4. The novel device was subjected to 15 hours of AM1 light, resulting in a shift of curve e to quantum efficiency curve f of FIG. 5. Some decrease in the quantum efficiency of the device within the spectral region of interest is evident in the shift, but the response remains comparable to that of the reference device.

The device producing curves e and f in FIG. 5 has an intrinsic amorphous silicon region about 500 nm in thickness. In the amorphous silicon art it is believed that the device efficiency decline over time attributed to the so-called Staebler-Wronski effect can be reduced by increasing the electric field in the light-absorbing intrinsic region. One method of increasing the field is reduction of the thickness of that region. A thinner intrinsic region also improves the current collection efficiency because the charge carriers have a shorter distance to travel before collection.

Additional embodiments of the invention having reduced thickness intrinsic regions were

prepared. In these devices, the thickness of the intrinsic region within the amorphous silicon body was reduced to about 250 nm. The thickness of the ITO layer was 20 nm. As noted above, very little difference in the quantity of ultraviolet light absorbed in the intrinsic region results when the thickness of that region is reduced to 250 nm from 500 nm.

The quantum efficiencies before and after light exposure are plotted in FIG. 6 for an example of the device having a 250 nm thick intrinsic region. Curve g is the measured quantum efficiency as a function of wavelength for the device, before significant solar light exposure. (Curve a is the efficiency of the reference gallium arsenide phosphide device.) After exposure of the device to AM1 radiation for 30 hours, the efficiency shifted to curve h. Thereafter, the device was exposed to ultraviolet light from a low pressure mercury vapor lamp for 20 hours. This exposure resulted in another shift to efficiency curve to i. Before measurement of curve i, a recalibration of the instrumentation was required. The recalibration introduced a small error that is large enough to account for the small variations between curves h and i. In other words, the device with the 250 nm intrinsic region exhibited a very stable quantum efficiency after extended solar and ultraviolet light exposure.

The measured results of FIGS. 4-6 demonstrate that the invention provides a photovoltaic

ultraviolet responsive device having quantum efficiencies and stability as good as or better than those of existing commercial devices, and at lower cost. The ultraviolet detector performs well because its front contact oxide film is kept very thin. The long term stability of the detector is enhanced in a p-i-n structure embodiment by minimizing the thickness of the intrinsic region.

Another schematic, sectional view of a photodetector 70 according to the invention is shown in FIG. 7. The photodetector 70 shown in FIG. 7 is similar to the photodetectors 10, 30 and 50 shown in FIGS. 1, 2 and 3, and includes electrical leads 11 and 12 for applying a bias voltage to the photodetector.

Photodetector 70 includes a body of disordered silicon 20 composed of three layers 21, 22 and 23. As indicated in FIG. 7, outside layers 21 and 22 are generally thinner than central layer 23, although FIG. 7 is not drawn to any scale and layer thicknesses are shown disproportionately for clarity. Disordered silicon body 20 forms a p-i-n diode of known structure. Layers 21 and 22 are intentionally doped and are of opposite conductivity types. That is, one of layers 21 and 22 is n-type and the other is p-type. Layer 23 is substantially intrinsic type, meaning that it has a relatively high resistivity and may be weakly n-type or p-type.

Body 20 lies between and contiguous to a front contact 24 and a rear contact 13. Front contact 24 is a transparent, electrically conductive oxide, such as indium tin oxide or tin oxide or films of both oxides. In the latter case, a thin film of tin oxide may be used to prevent diffusion of indium from indium tin oxide into body 20. Contact 13 may also be a thin layer of a transparent, electrically conductive oxide or may be a metal, such as stainless steel. In the former case, a substrate 14 provides support for photodetector 70. As seen in FIG. 7, layers 22, 23 and 21 are arranged serially on front contact 24, transversely to the direction of incident light that enters body 20 through contact 24.

In the foregoing and following discussion, the terms disordered silicon and amorphous silicon are used. As understood by those of skill in the art, microcrystalline and amorphous silicon are useful in electronic devices only when an element or elements for electronically passivating dangling bonds is included. Examples of passivating elements that may be present separately or in combination are hydrogen and fluorine. The term light as used in this description refers broadly to electromagnetic radiation extending from the UV region (wavelengths of about 200 nanometers or more) through the infrared region (wavelengths up to about 1 micron) and is not limited to the visible spectrum.

As previously described, the thickness of front contact 24 can dramatically affect the spectral response of photodetector 70. As disclosed there, in order for photodetector 70 to respond desirably to UV light, front contact 24 should be thinner than about 30 nanometers (nm). Thicker layers of a transparent, electrically conductive oxide may be used in photodetector 70 when visible and/or infrared light is desired to be detected, without concern for detecting UV light. In those instances, front contact 24 should be thicker than 30 nm and should preferably be 60 to 80 nm in thickness.

The thickness of layer 22 affects the amount of incident light transmitted through front contact 24 to intrinsic layer 23. When photodetector 70 is employed as a detector of UV and/or visible light, the thickness of layer 22 is preferably between about 5 and 22 nm. When photodetector 70 is employed for detecting visible light, without regard to detection of UV light, layer 22 may be 10 to 30 nm in thickness.

The light transmission of layer 22 may be altered by controlling the structure of layer 22 or by adding an alloying element to it. In the former case, layer 22 may be microcrystalline silicon, which is known to have a higher light transmissivity than its amorphous silicon counterpart. Microcrystalline silicon is considered disordered, but not as disordered as amorphous silicon. In the latter case, if

layer 22 is amorphous silicon, an energy band gap altering alloying element such as germanium, nitrogen or carbon may be added. Germanium reduces the energy gap so that less light is transmitted. By contrast, nitrogen and carbon widen the energy gap improving light transmission.

In layer 23, charge carriers are created that produce a current indicating the presence of incident light. The quantity of charge carriers produced indicates the intensity of incident light. Intrinsic layer 23 is made much thicker than layers 21 and 22 in order to absorb incident light efficiently. Layer 23 may be 100 to 500 nm in thickness, and is preferably 200 to 300 nm in thickness, in a photodetector intended for use in the UV to visible light spectral regions. Since the light absorption of amorphous silicon decreases with the energy of the incident light, in a photodetector intended for visible to infrared detection, layer 23 may have a thickness of 200 nm to 1 micron. The thickness of layer 21 is less critical than the other thicknesses, since most of the incident light is absorbed in layer 23.

Examples of the spectral response performance of photodetectors according to the invention and intended for high quality UV response are disclosed above. The low noise performance of similar devices was determined from various measured characteristics that do not depend on incident light or the particular

spectral response characteristics of photodetectors according to the invention. The noise performance of the novel photodetectors was compared to results obtained for commercially available crystalline silicon photodetectors and for gallium arsenide phosphide Schottky barrier UV photodetectors.

In FIG. 8, the dark current density (J) versus voltage response curves for a photodetector according to the invention (curve A), for a crystalline silicon photodetector (curve B) and for a Hamamatsu Schottky barrier photodetector (curve C), are plotted. The photodetector according to the invention for which responses are disclosed in FIGS. 8-10 was constructed from amorphous silicon and included doped layers approximately 12 to 15 nm in thickness and a substantially intrinsic central layer approximately 250 nm in thickness. Because the measurements described were made without incident light, the thickness of the front contact is not a significant parameter. In the photodetector reported, the front contact was a film of indium tin oxide approximately 15 to 20 nm in thickness and the second contact was a tin oxide film. The tin oxide film was deposited on a glass substrate. As shown in FIG. 8, the reverse saturation current of the novel photodetector (A) is about one order of magnitude smaller than that of a crystalline silicon photodetector (B) and more

than two orders of magnitude lower than that of the Schottky barrier photodetector (C).

In FIG. 9, the current versus reverse bias voltage characteristic for the photodetector according to the invention is plotted as a function of temperature. The information provided in FIG. 9 is important in calculating the noise characteristics of the novel photodetector. In FIG. 10, the current flowing through a photodetector according to the invention under various reverse bias voltages is plotted against the inverse temperature of the photodetector. FIG. 10 shows that the activation energy of the amorphous silicon photodetector is about 0.85 electron volts, which is approximately one-half of the energy band gap of hydrogenated amorphous silicon. The information plotted in FIG. 9 indicates that the dominant current mechanism in a reverse bias photodetector according to the invention is a generation-recombination current. This result, compared with that for crystalline silicon, is consistent with the wider energy band gap of amorphous silicon that discourages the diffusion current mechanism.

From the measured characteristics of FIGS. 8-10, the noise characteristics of the novel photodetectors can be calculated and compared to those of crystalline silicon and Schottky barrier photodetectors. In FIG. 11, an equivalent circuit employing a photodetector in combination with an amplifier and

filter for calculation of noise characteristics is schematically shown. Photodetector 90 comprises an ideal diode 91 electrically connected in parallel with a resistor 92 and a capacitor 93. Resistor and capacitor 92 and 93 represent equivalent electrical elements that are characteristic of an actual photodiode. Amplifier 94 is preferably an operational amplifier. For the described noise calculations, the characteristics of a Burr-Brown 3528 CM amplifier were selected for amplifier 94. A feedback resistor 95 connects the output terminal of amplifier 94 with its negative sense input terminal. A filter 96 having sharp cutoff frequencies is connected to the output terminal of amplifier 94. The noise is measured at the output of filter 96 which permits selection of various sampling bandwidths.

For the operational amplifier employed in the noise calculations, the input bias current is 75 femtoamperes and the input resistance is 10^{13} ohms. The input capacitance of the amplifier is 0.8 picofarads. The input voltage noise of the operational amplifier in the 1/frequency regime is equal to the inherent noise voltage of the amplifier divided by the square root of the frequency raised to a power of 1.13. The input noise voltage of the amplifier selected is about 475 nanovolts. Feedback resistor 95 was chosen as 10^{10} ohms so that the circuit was directed specifically at low light level detection.

Under the conditions chosen, shot noise in the photocurrent, in the amplifier input current and in the amplifier voltage are all negligible. Based on that assumption, the only noise sources are Johnson noise in feedback resistor 95, Johnson noise in the zero bias resistance of the photodiode, interaction of the amplifier noise with the input capacitance and interaction of the amplifier voltage noise with the input resistance.

In the comparison, a crystalline silicon EG&G UV-215BQ detector which has an active area of about 5 mm^2 was chosen. The equivalent resistance of the EG&G photodetector is 2×10^8 ohms at 22°C. Its input capacitance is 150 picofarads. The Hamamatsu G1126-02 gallium arsenide phosphide photodiode has a similar active area and an equivalent resistance of 2.1×10^{10} ohms at 22°C and an input capacitance of 1.8 nanofarads. The equivalent resistance of the novel photodetector was obtained by extending the 10 millivolt curve of FIG. 10 to 22°C to calculate the equivalent resistance, which was 5.5×10^{11} ohms. The measured input capacitance of the novel photodetector was 4.2 nanofarads.

In making the noise calculations, the equivalent resistance of the crystalline silicon and Schottky barrier photodiode was assumed, based on actual measurements, to decrease by a factor of 10 for each 20°C rise in the temperature of the diode.

Changes in the equivalent resistance of the novel photodetector were obtained from FIG. 10. FIG. 10 indicates that each 20°C increase in temperature results in a decrease by a factor of six of the equivalent resistance of the novel photodetector. Further, it is assumed that the equivalent capacitance of all the photodiodes is independent of temperature and frequency.

The root mean square (rms) noise current of the novel photodetector (curve A) and of the crystalline silicon (curve B) and gallium arsenide (curve C) photodetectors are plotted in FIGS. 12A and 12B as a function of temperature for two different bandwidths of filter 96 of FIG. 11. In FIG. 12A the bandwidth is 0.1 Hertz (Hz) and in FIG. 12B the bandwidth is 1.0 Hz. FIGS. 12A and 12B show that, in contrast to the known photodetectors, the noise current in the novel photodetector is essentially independent of temperature in the range from about 22°C (room temperature) to 80°C. In every case, the noise current is of the novel photodetector substantially below that of crystalline silicon. A significant advantage is also obtained over the Schottky barrier photodetector at elevated temperatures. The performance of the novel photodetector is clearly superior to that of the gallium arsenide phosphide diode at temperatures of 60°C and higher. As the bandwidth of filter 96 is reduced, the temperature at which the advantage of the

novel photodetector over the Schottky barrier photodetector occurs is significantly reduced.

The calculations that produced the results shown in FIGS. 12A and 12B assume that the capacitance of the novel photodetector is independent of frequency and temperature. However, it is known that so-called traps lying within the energy band gap of amorphous silicon will cause the capacitance of the novel photodetector to follow a modulated signal if the frequency of that signal is low and the device temperature is relatively high. We found that the capacitance of the novel photodetector changed from 4.2 nanofarads at 1 kHz and 22°C to 5.9 nanofarads at 1 Hz and 80°C. When this change in capacitance is taken into account, the 80°C point on curve A in FIG. 12B changes to the point marked with an x. The correction is a small one, indicating that the results of FIGS. 12A and 12B are reliable.

The chosen amplifier 94 exhibited a relatively amplifiers having lower noise voltages can be chosen so that still better performance of the novel photodetector can be realized. In practice, it is preferable to mount the amplifier, preferably as an integrated circuit chip, and the photodetector on the same mounting body. In that arrangement, the interconnections between the amplifier and photodetector can be kept short to avoid receiving additional noise. In addition, use of the same mounting body means that

the amplifier and photodetector will be in thermal communication and will be maintained at similar temperatures, reducing another potential noise source. The amplifier is not limited to an operational amplifier, but may be a preamplifier. and even a digital amplifier.

The invention has been described with respect to certain preferred embodiments. Various modifications and additions within the spirit of the invention will occur to those of skill in the art. Accordingly, the scope of the invention is limited solely by the following claims.

CLAIMS

1. A photovoltaic device responsive to incident energy in the ultraviolet range of the electromagnetic spectrum comprising:

an at least partially electrically conductive layer, a body of amorphous silicon disposed on said layer, and a thin film of an electrically conductive, light-transmissive oxide for receiving incident light disposed on said amorphous body opposite said layer, said light-transmissive oxide film having a thickness of less than about 30 nm.

2. The device of claim 1 wherein said oxide film is chosen from the group consisting of indium oxide doped with tin and tin oxide.

3. The photovoltaic device of claim 1 wherein said oxide layer has a thickness of at least about 15 nm.

4. The device of claim 1 wherein said body of amorphous silicon includes an essentially intrinsic region sandwiched between p-type and n-type regions, said three regions being disposed on said layer for serial passage of light through them.

5. The device of claim 4 wherein said intrinsic region has a thickness of no more than about 500 nm.

6. The device of claim 4 wherein said intrinsic region has a thickness of no more than about 250 nm.

7. The device of claim 4 wherein the region of said amorphous silicon body in contact with said oxide film comprises microcrystalline amorphous silicon.

8. The device of claim 4 wherein the region of said amorphous silicon body in contact with said oxide film contains a band gap increasing agent consisting of one of carbon and nitrogen.

9. The device of claim 1 wherein said layer comprises a substrate providing mechanical support for the device.

10. The device of claim 9 wherein said substrate comprises glass coated with an electrically conducting film.

11. THe device of claim 9 wherein said substrate is selected from the group consisting of metals, metallic alloys, and silicon.

12. The device of claim 1 wherein said body of amorphous silicon comprises a doped film of one of p-type and n-type conductivities and said layer is crystalline silicon doped oppositely from said amorphous silicon.

13. The device of claim 12 wherein said doped amorphous silicon film is n-type and said crystalline silicon is p-type.

14. The device of claim 12 wherein said amorphous silicon film is microcrystalline silicon.

15. The device of claim 12 wherein said amorphous silicon film contains a band gap increasing agent consisting of one of carbon and nitrogen.

16. The device of claim 1 including a second transparent film disposed on said oxide film opposite said amorphous silicon body for altering the optical interference characteristics of said oxide film alone.

17. The device of claim 16 wherein said second transparent film is selected from the group consisting of silicon dioxide, silicon nitride, magnesium fluoride, and calcium fluoride.

18. The device of claim 16 including a third transparent film disposed on said second transparent film opposite said oxide film for altering the optical interference characteristics of said oxide film and second transparent film together.

19. The device of claim 1 including a metallic current collector disposed on a portion of the oxide film.

20. The device of claim 1 including an ultraviolet light-transmitting glass substrate contacting said oxide film.

21. The device of claim 20 wherein said glass substrate is quartz.

22. The device of claim 20 wherein said oxide film is tin oxide.

23. The device of claim 20 wherein said body of amorphous silicon includes an essentially intrinsic region sandwiched between p-type and n-type regions, said three regions being disposed on said film for serial passage of light through them.

24. The device of claim 23 wherein the region in contact with said oxide film contains a band gap increasing agent consisting of one of carbon and nitrogen.

25. The device of claim 23 wherein said intrinsic region has a thickness of no more than about 500 nm.

26. The device of claim 23 wherein said intrinsic region has a thickness of no more than about 250 nm.

27. The device of claim 20 including a second transparent film disposed on said substrate opposite said oxide film for altering the optical interference characteristics of said glass substrate alone.

28. The device of claim 27 wherein said second transparent film is selected from the group consisting of magnesium fluoride and calcium fluoride.

29. The device of claim 27 including a third transparent film disposed on said second transparent film opposite said glass substrate for altering the optical interference characteristics of said glass and second transparent film together.

30. A method of detecting relatively weak light signals comprising employing as a photodetector a semiconductor diode including a transparent, electrically conductive oxide, on which light is incident, as a first contact, a disordered silicon body including three layers serially disposed on said first contact transversely to the direction of incident light, the two outer layers being n-type and p-type, respectively, and the central layer being of substantially intrinsic conductivity type, and a second contact disposed on said silicon body opposite said first contact, impressing a reverse bias voltage across said silicon body through said first and second contacts, and measuring changes in the current flowing through said reverse biased diode in reference to said current flow when the biased diode is not illuminated.

31. The method of claim 30 wherein said silicon body includes a microcrystalline silicon layer contiguous to said front contact and said other two layers are amorphous silicon.

32. The method of claim 30 wherein said body includes an amorphous silicon alloy in said layer contiguous to said front contact, said alloy containing one of germanium, carbon, and nitrogen to modify the energy band gap and spectral response of said diode.

33. The method of claim 30 wherein said silicon body is composed of amorphous silicon.

34. The method of claim 33 including adjusting the thickness of said layer contiguous to said first contact to transmit most of the incident energy in a selected spectral region to said substantially intrinsic layer.

35. The method of claim 34 including detecting ultraviolet light wherein the thickness of said layer contiguous to said first contact is adjusted to less than about 20 nanometers.

36. The method of claim 30 including adjusting the thickness of the front contact to improve the response of the photodetector in a selected spectral region.

37. The method of claim 36 including detecting ultraviolet light wherein the thickness of said front contact is adjusted to less than 30 nanometers.

38. The method of claim 30 including amplifying said changes in the current flow with an amplifier.

39. The method of claim 38 including mounting the amplifier and photodetector on the same mounting body to reduce the length of interconnections between the amplifier and photodetector and to maintain the photodetector and the amplifier at similar temperatures.

40. The method of claim 30 wherein the temperature of said diode is greater than about 40°C.

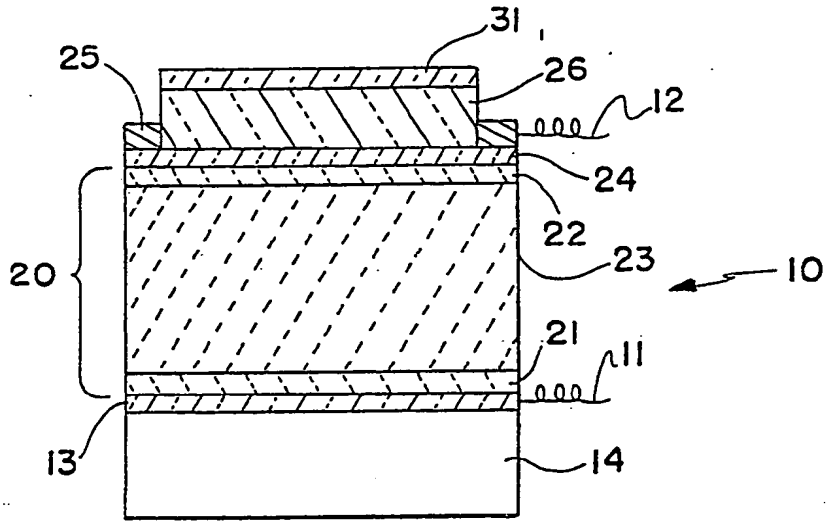


FIG. 1

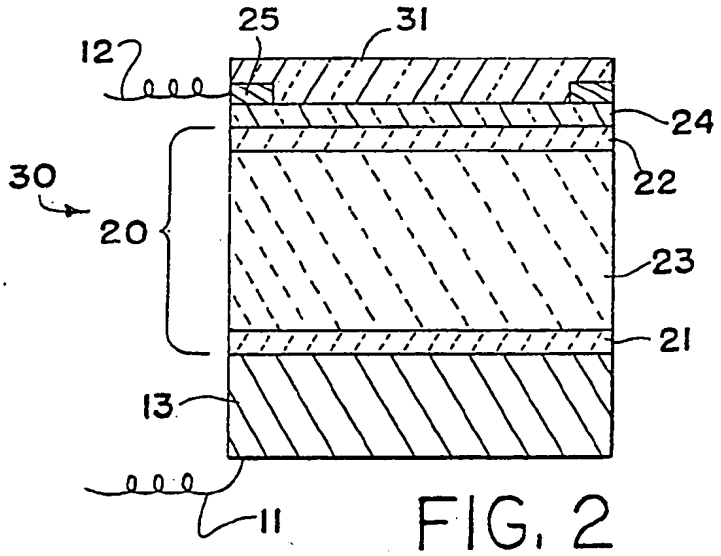


FIG. 2

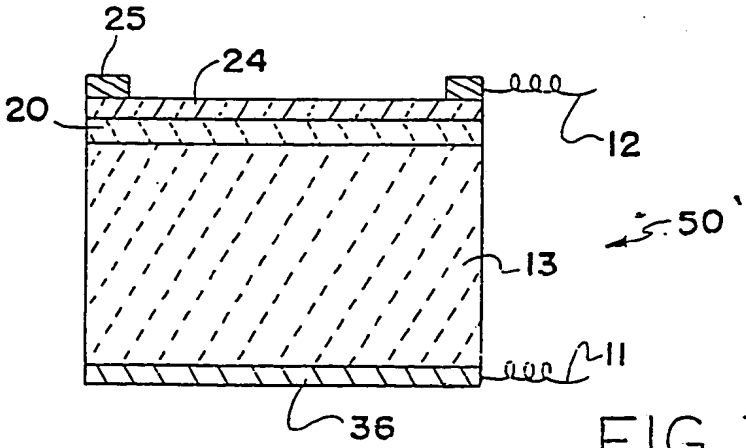


FIG. 3

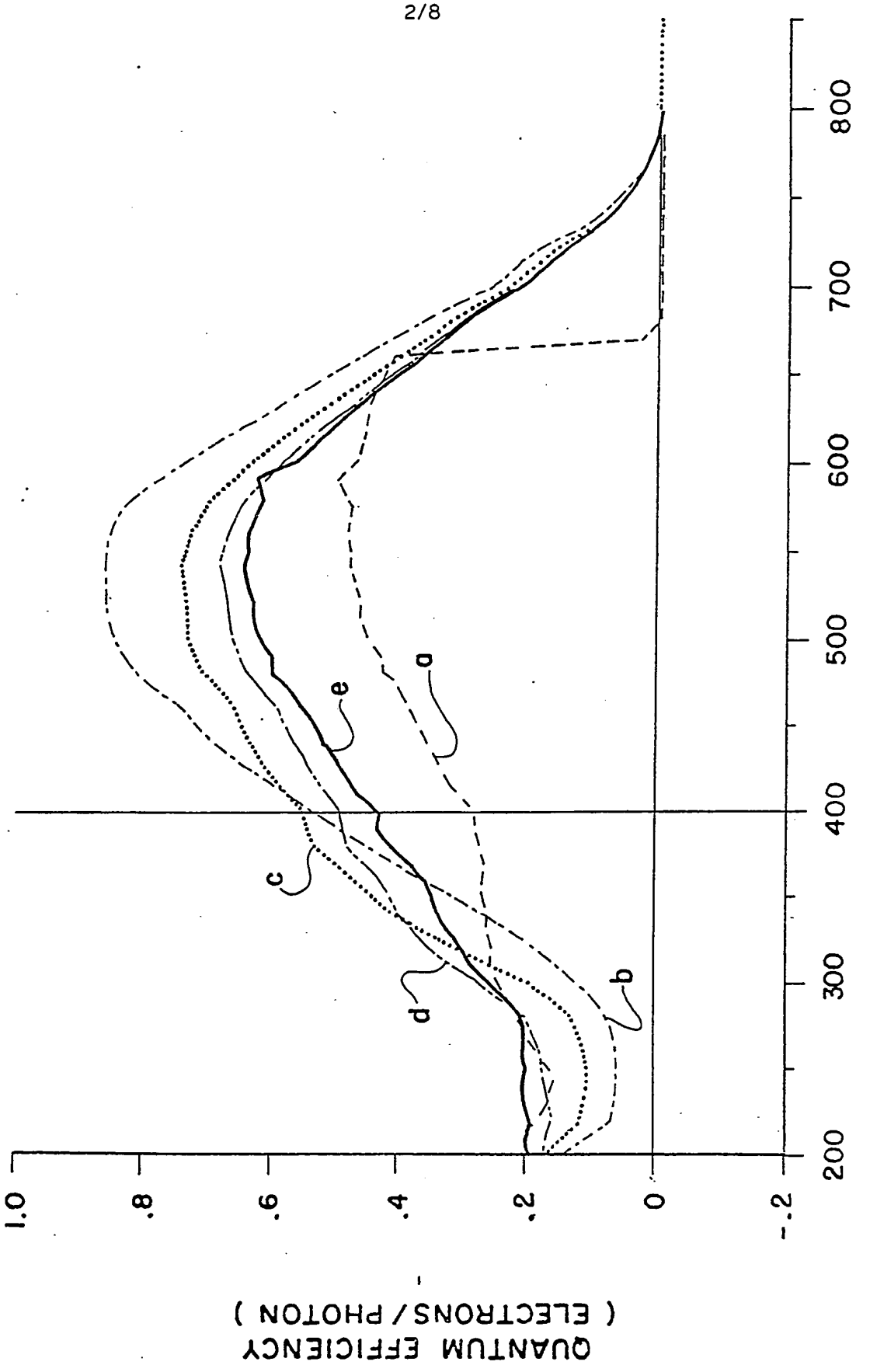
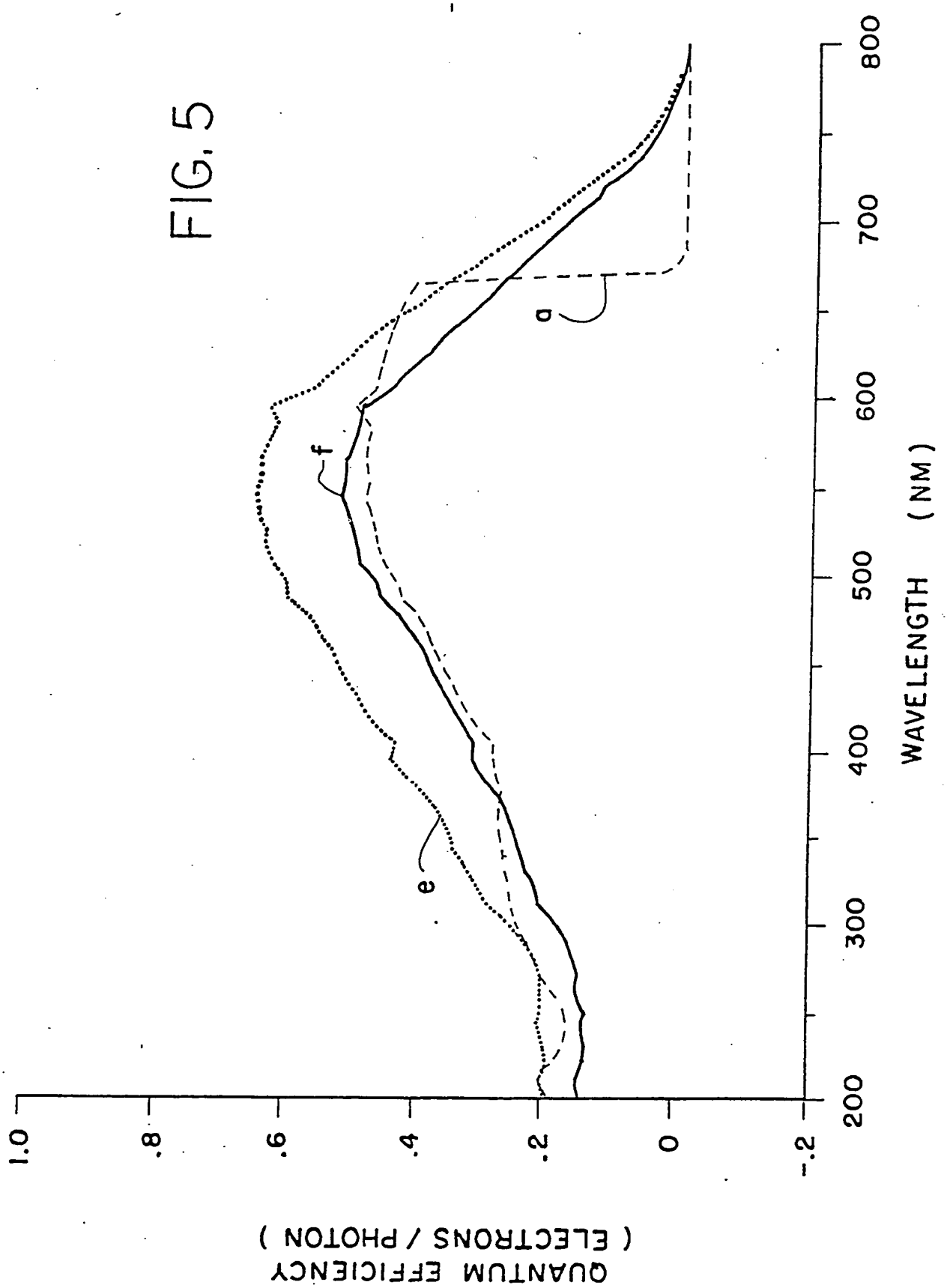

QUANTUM EFFICIENCY
(ELECTRONS / PHOTON)
1.0
.8
.6
.4
.2
0
-.2
200
300
400
500
600
700
800
WAVELENGTH (NM)
a
b
c
d
e

FIG. 4

FIG. 5


QUANTUM EFFICIENCY
(ELECTRONS / PHOTON)
1.0
.8
.6
.4
.2
0
-.2
200
300
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500
600
700
800
WAVELENGTH (NM)
a
e
f

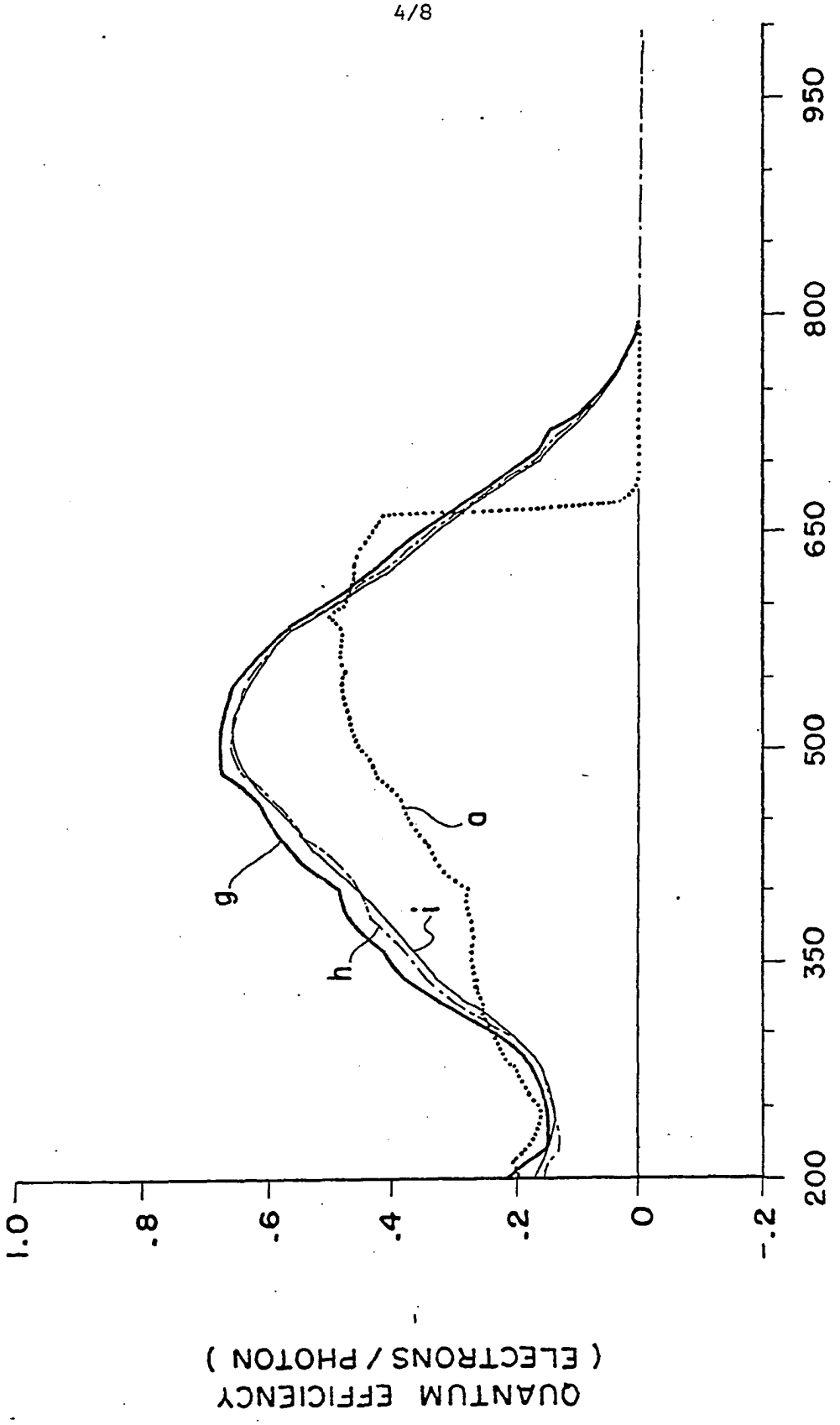
QUANTUM EFFICIENCY
(ELECTRONS / PHOTON)
1.0
.8
.6
.4
.2
0
-.2
200
350
500
650
800
950
WAVELENGTH (NM)
a
g
h
i

FIG. 6

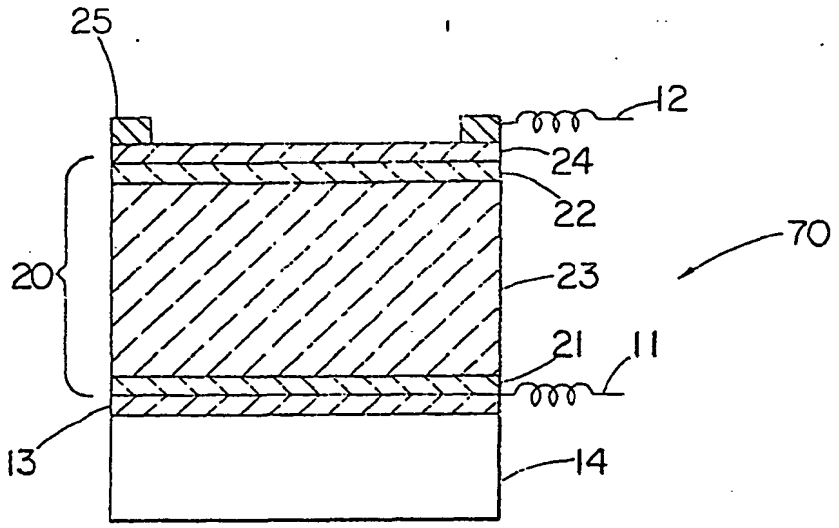
25
12
24
22
70
20
23
21
11
13
14

Fig. 7

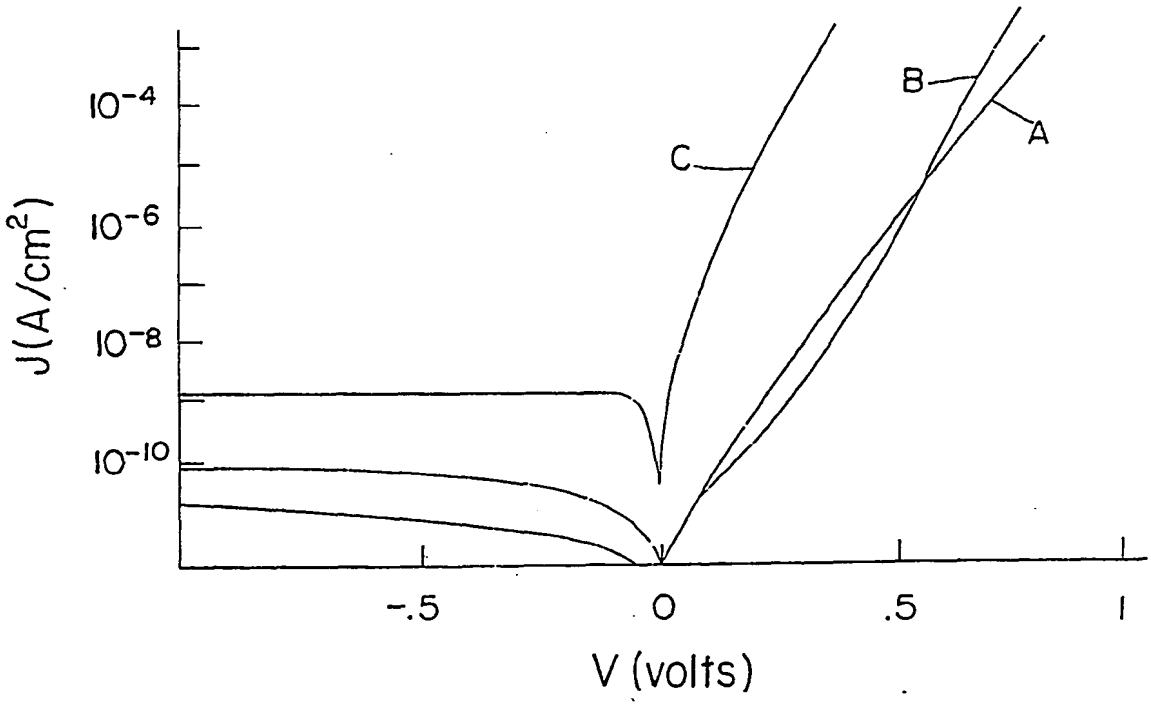
B
A
C
10^{-4}
10^{-6}
10^{-8}
10^{-10}
J(A/cm^2)
-.5
0
.5
1
V (volts)

Fig. 8

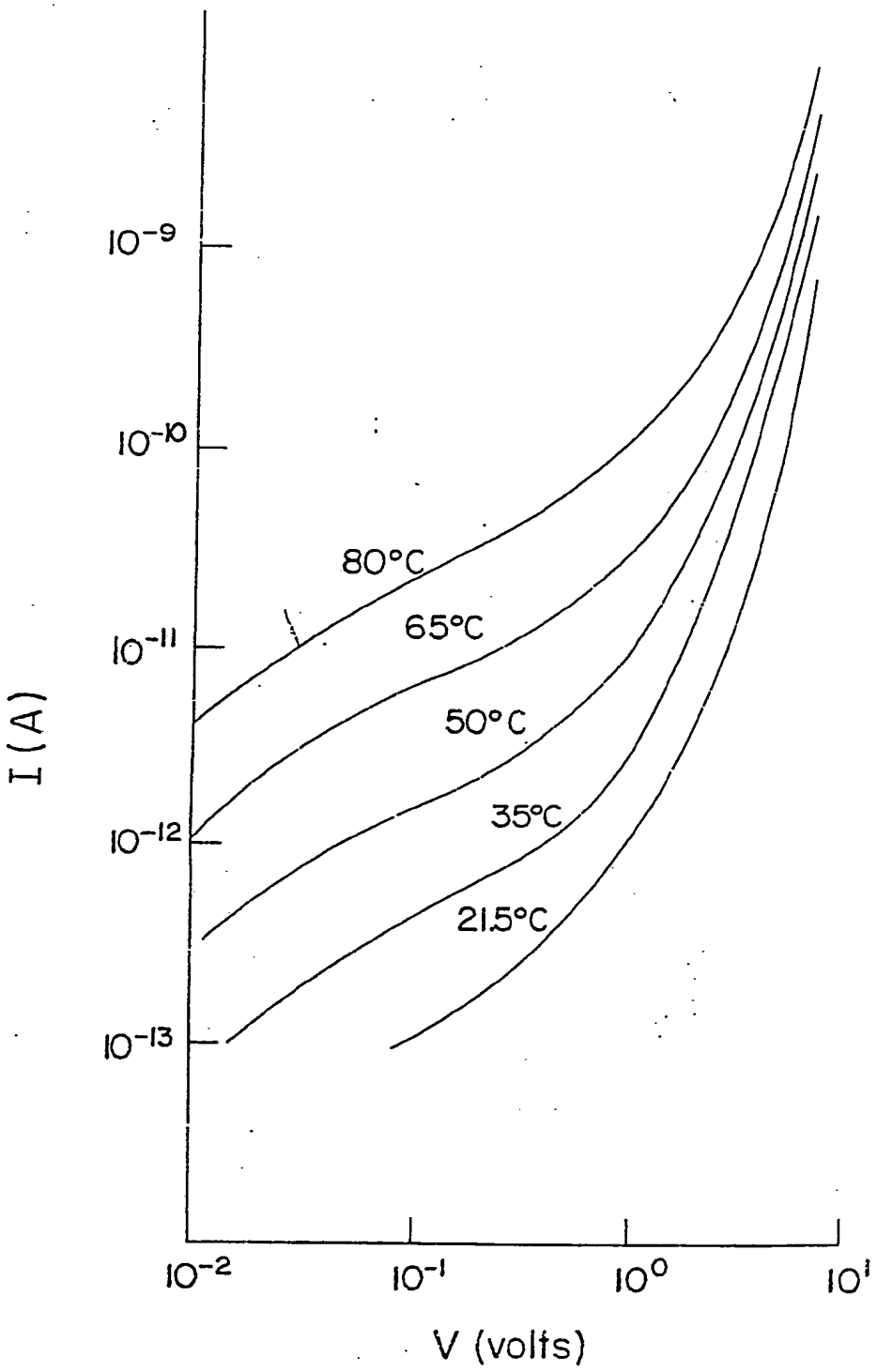
10^{-9}
10^{-10}
10^{-11}
10^{-12}
10^{-13}
I (A)
80°C
65°C
50°C
35°C
21.5°C
10^{-2}
10^{-1}
10^{0}
10^{1}
V (volts)

Fig. 9

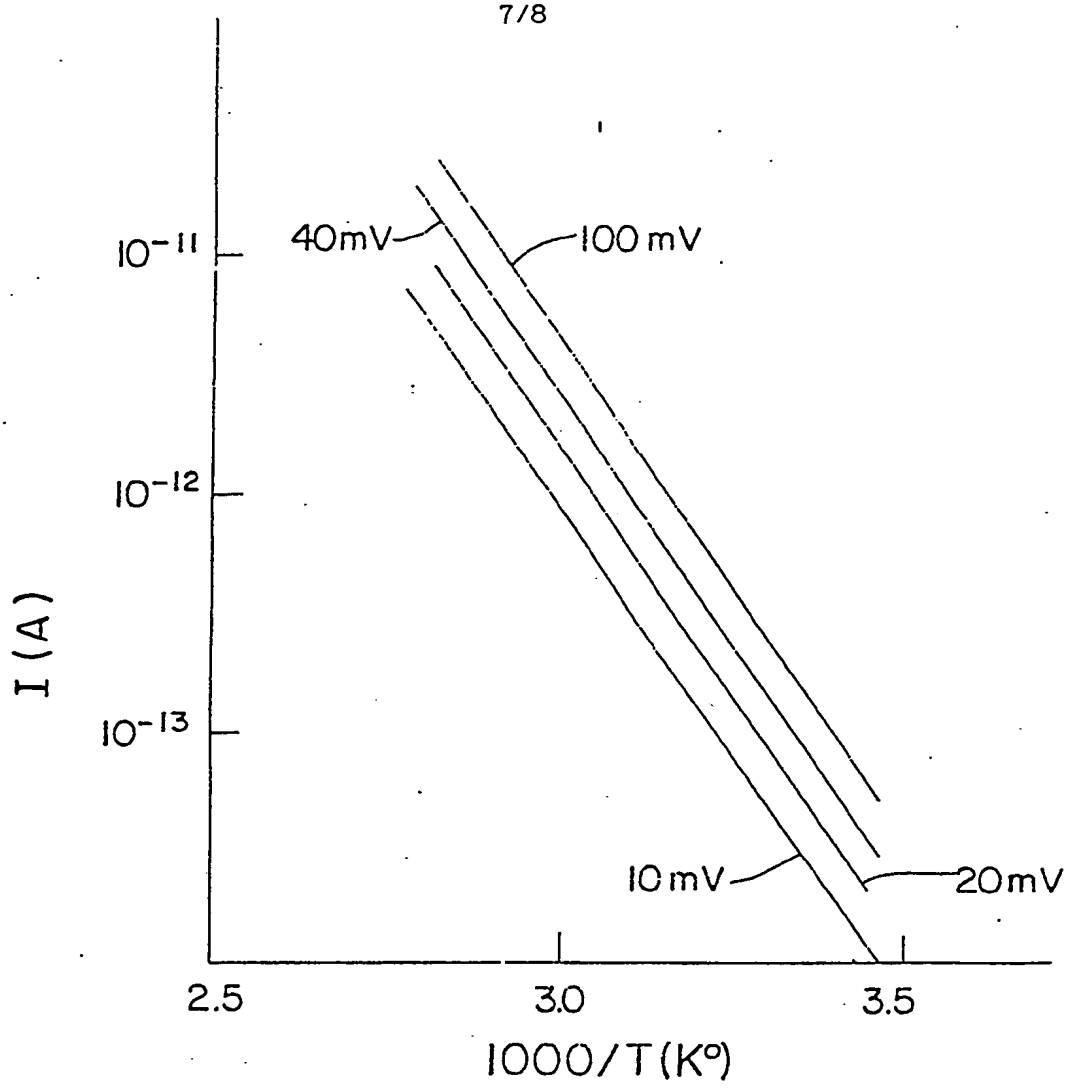
40mV
100 mV
10 mV
20mV
10^{-11}
10^{-12}
10^{-13}
I (A)
2.5
3.0
3.5
1000/T (K°)

Fig. 10

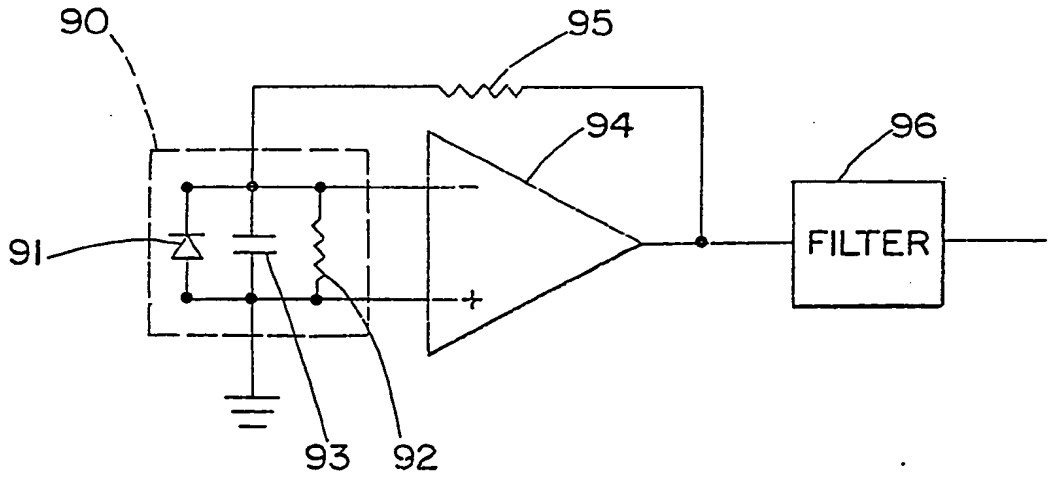
90
95
94
96
91
FILTER
93
92

Fig. 11

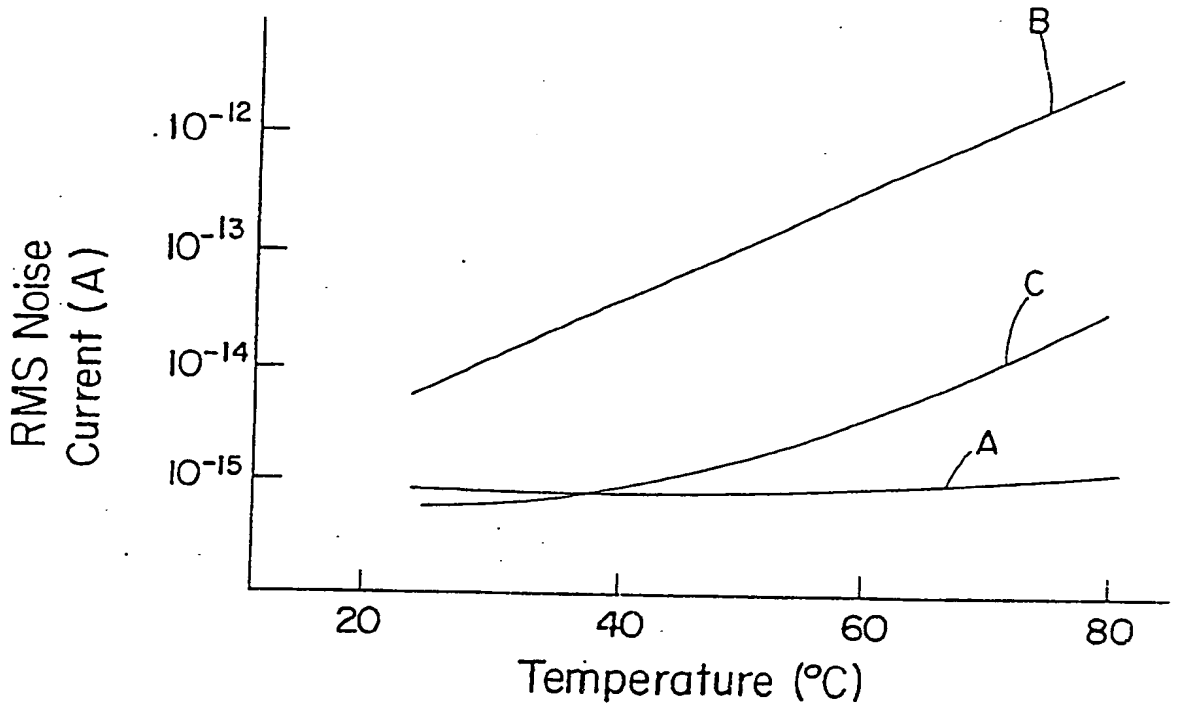

Fig. 12A

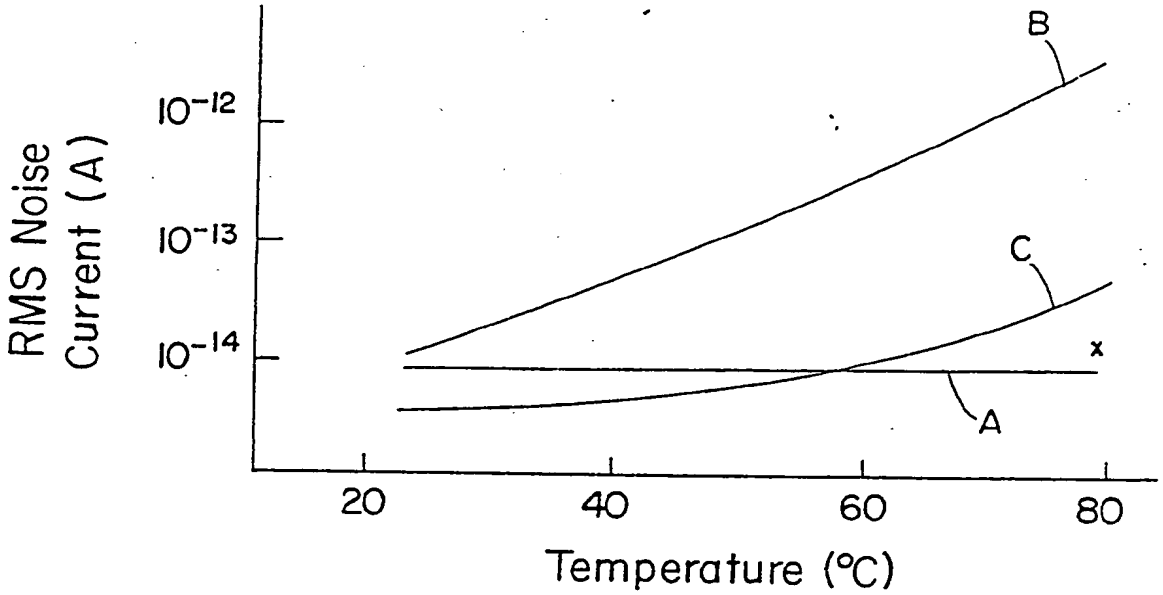

Fig. 12B

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US88/03579

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[4] H01L 31/02, 31/10; G01J 1/42

U.S. CL. 136/258AM; 250/372

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
U.S. CL.	136/256, 258AM 357/30K, 30P, 30Q 250/370 - 372

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A, E Y, E	US,A 4,784,702 (HENRI) 15 November 1988 (15.11.88) (Note Col. 3, lines 21-22 for transparent conducting layer thickness)	1-29 30-36, 38
A Y	US,A, 4,532,537 (KANE) 30 July 1985 (30.07.85) (Note Col. 2, lines 30-35 for P-I-N structure)	1-29 30-36, 38
A	US,A, 4,476,346 (TAWADA ET AL) 09 October 1984 (09.10.84)	2, 4-15, 23-26
Y	US,A, 4,233,514 (KINGSLEY) 11 November 1980 (11.11.80) (Note Figure 1)	30-36, 38
Y	US,A, 4,703,336 (OVSHINSKY ET AL) 27 October 1987 (27.10.87) (Note Figure 4 and Col. 16, lines 17-39)	30-36, 38

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

01 December 1988

Date of Mailing of this International Search Report

11 JAN 1989

International Searching Authority

ISA/US

Signature of Authorized Officer

Aaron Weisstuch

Aaron Weisstuch

International Application No. PCT/US88/03579

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [1]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers , because they relate to subject matter [2] not required to be searched by this Authority, namely:

2. ☐ Claim numbers , because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [3], specifically:

3. ☐ Claim numbers_____, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [2]

This International Searching Authority found multiple inventions in this international application as follows:

Group I, Claims 1-29, drawn to a photovoltaic device
Group II, Claims 30-38, drawn to a method of light detection

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application. Telephone practice

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.

Group I, Claims 1-29, drawn to a photovoltaic device having a particular thickness of its transparent conductive oxide (TCO) layer, constitutes a single general inventive concept.

Group II, Claims 30-38, drawn to a method of detecting light by means of reverse biasing of a p-i-n type device, constitute a different general inventive concept from that of claims 1-29 because the majority of the Group II claims do not require the particular thickness of the TCO layer of the Group I claims and the device of the Group I claims has separate utility as an electricity generating source (e.g. as a solar cell) in addition to use as a light detector in a reverse biased mode.